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(71) Applicant: THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Midland, MI 48674 (US).

(72) Inventors: HAHNFELD, Jerry, L.; 920 Scenic Drive, Midland, MI 48642 (US). PARSONS, Gary, D.; 5016 Redfern Circle, Midland, MI 48642 (US). JONES, Mary, Ann; 34 Greenlawn Drive, Midland, MI 48640 (US).

(74) Agent: ZETTLER, Lynn, M.; Intellectual Property, P.O. Box 1967, Midland, MI 48641-1967 (US).

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(54) Title: HIGH DATA DENSITY OPTICAL MEDIA DISCS

(57) Abstract: A high data density pre-recorded optical media disc having a data density of at least 7.5 Gigabytes per disc layer or 0.17 Gigabytes per square cm (Gb/cm²) per layer and a degree or replication such that the average pit depth equals 1/4 to 1/8 times (the wavelength of the laser divided by the refractive index of the disc); or a rewritable optical media disc having a data density of at least 0.05 Gb/cm², wherein at least 75 percent replication is achieved as measured by a combination of groove height and the left and right sidewall angles, and wherein the pre-recorded or rewritable disc has a retardation of less than 25 nm per 0.6 mm substrate thickness, and a water absorbance of less than 0.5 percent as measured according to ASTM D570.

HIGH DATA DENSITY OPTICAL MEDIA DISCS

The present invention relates to optical media discs.

5 Optical media discs typically comprise a plastic substrate(s) which holds laser readable data and have been traditionally produced from polycarbonate resins. Such discs include compact discs, video discs, DVD discs, CD-rewriteable discs, optical magnetic discs and optical cards. The capacity of the disc to hold information is referred to as the data density. Typical data densities of the polycarbonate discs of the current art are less than 5 Gigabytes per substrate layer in prerecorded formats, wherein several substrate layers can be combined to make a higher data density disc.

10 However, polycarbonate has several disadvantages, including the need for mold release agents in order to prevent pit deformation caused by adherence of the polymer to the nickel stamper used in disc production. The prevention of pit deformation becomes increasingly difficult at higher data densities and can cause reading errors. Additionally, polycarbonate has a high level of water absorbency, which causes dimensional instability or warping of the disc, thus requiring vapor barrier layers.

15 Data densities of greater than 5 Gigabytes per substrate layer have not been achieved in the current art due to a number of problems, including poor pit replication, birefringence, dimensional stability, resin processability and mold release.

Therefore, there remains a need for higher data density optical media discs having good pit replication, low birefringence, good dimensional stability, resin processability and mold release

20 properties.

The present invention is a high data density pre-recorded optical media disc having a data density of at least 7.5 Gigabytes per disc layer or 0.17 Gigabytes per square cm (Gb/cm^2) per layer and a degree of replication such that the average pit depth equals 1/4 to 1/8 times (the wavelength of the laser divided by the refractive index of the disc) and wherein the disc has a retardation of less than 25

25 nm per 0.6 mm substrate thickness, and a water absorbance of less than 0.5 percent as measured according to ASTM D570.

Another aspect of the present invention is a high data density rewritable optical media disc having a data density of at least 0.05 Gb/cm^2, wherein at least 75 percent replication is achieved as measured by pit depth and left and right sidewall angles, and wherein the disc has a retardation of less

30 than 25 nm per 0.6 mm substrate thickness, and a water absorbance of less than 0.5 percent as measured according to ASTM D570.

The discs of the present invention are unique in the combination of their high data density and excellent properties including low birefringence, high transparency, low water absorption, good dimensional stability, and excellent surface replication.

35 One aspect of the present invention is a prerecorded high data density optical media disc. High data density, in the case of pre-recorded formats, refers to a capacity of at least 0.17 Gb/cm^2 per substrate surface or layer. The data density is the data storage capacity per square area of a substrate layer. Generally, the data density will be at least 0.2, typically at least 0.22, advantageously at least 0.24, preferably at least 0.26, more preferably at least 0.27, even more preferably at least 0.28,

40 and most preferably at least 0.3 Gb/cm^2, per substrate surface or layer. In a preferred embodiment,

two or more layers can be combined to form a single disc having increased data density due to the accumulated data densities of the layers.

Another aspect of the present invention is a rewritable optical media disc having a data density of at least 0.05 Gb/cm^2, generally at least 0.06, preferably at least 0.07, more preferably at least 0.075, and most preferably at least 0.08 Gb/cm^2. Rewriteable discs comprise a polymer substrate which has a series of tracks or grooves molded into the surface where information can be deposited.

The amount of data density refers to the data density as measured only over the data containing area of the disc. Methods of measuring data density are well known in the art.

Replication is important in pre-recorded optical media discs in that insufficient replication will render the disc unreadable. Therefore, the replication must be sufficient such that the disc is readable or writeable. Typically, this is achieved by obtaining a pit depth equal to n times the wavelength of the reader laser used, divided by the refractive index of the substrate material, represented by the formula:

Pit depth = n x (wavelength/refractive index).

For adequate replication in such formats, n is typically between 1/4 and 1/8, preferably between 1/4 and 1/7 and most preferably between 1/4 and 1/6. The laser used in reading discs of such high densities can be a laser having a wavelength of less than 630 nm and is typically a blue laser having a wavelength of from 380 to 410 nm. This information is well understood by those skilled in the art and disclosed the Compact Disc Handbook, 2nd Edition, by Pohlmann, pg. 55. This relationship described is necessary in order to translate encoded information on the disc to a bit stream thus making the disc readable.

Typically, at least 75 percent, preferably at least 80 percent, more preferably at least 85 percent and most preferably at least 90 percent replication is achieved in the high density optical media discs of the present invention. Replication refers to a process by which pits and/or a groove (surface features) are manufactured in the disc from a stamper. A stamper is a type of mold which contains the pit design carrying information in the case of pre-recorded discs or the groove design capable of holding information in the case of a rewriteable disc. Stampers used for pre-recorded discs contain columns having specified height, and left and right sidewall angles. The sidewall angle refers to the draft angle of the stamper surface feature(s). A column of the stamper forms a pit within the disc having a pit depth near or equal to the column height of the stamper and pit sidewall angles near or equal to the column draft angles. For rewritable discs, the stampers contain a surface feature capable of producing a groove having a specified groove depth, left and right draft angles as described previously. Replication for rewritable discs can best be distinguished by the successful transfer of groove height and sidewall angles from the stamper to the disc. Preferably, high replication is achieved as measured by the pit or groove depth and the left and right sidewall angles. In other words, the pit or groove depth and sidewall angles are at least a value which is 75 percent of the value measured in the stamper.

Methods of measuring pit depth, sidewall angles and general disc geography are well known by those in the art and include Atomic Force Microscopy.

The high data density optical media disc of the present invention has a retardation of less than 25 nm per 0.6 mm substrate (birefringence of less than 0.000042), and a water absorbance of less

than 0.05% as measured according to ASTM D 570. Retardation is measured by placing a molded DVD disc substrate between crossed polarizers and quarter wave plates (oriented in opposition). The retardation is measured 20 mm from the injection gate of the disc using light from a 633 nm laser. Transmitted intensity is measured and the retardation calculated using the following formula:

5
$$I = I0 \sin2((\pi/\lambda(\Delta nd)))$$

where Retardation = Δnd

Measured intensity = I

Incident intensity = $I0$

Wavelength = λ

10

The birefringence is calculated from the measured retardation by dividing retardation by the thickness of the substrate. Preferably the retardation is less than 20 nm, more preferably less than 15 nm and most preferably less than 10 nm in a disc substrate which is 0.6 mm thick. The water absorbance is preferably less than 0.04 percent, more preferably less than 0.02 percent and most

15   preferably less than 0.01 percent.

The discs of the present invention can be produced from any polymer which will successfully produce a high data density disc having the aforementioned properties, wherein the polymer also has:

a glass transition temperature (Tg) of greater than 110°C as measured by Differential Scanning Calorimetry (DSC) at 10°C/min.,

20   an elastic modulus (G') of less than or equal to 1000 dynes/cm^2 at a temperature of 240°C, preferably at 225°C, more preferably at 215°C and most preferably at 210°C, as measured by Dynamic Mechanical Spectroscopy measurements at a temperature ramp rate of 3°C/min., and a shear rate of 1 radian/sec using a parallel plate geometry (under nitrogen), and

a complex viscosity (Eta*) of less than 2000 poise, preferably less than 1300 poise, and more

25   preferably less than 600 poise, as measured according to Dynamic Mechanical Spectroscopy measurements, using shear rate sweeps at 280°C, and a shear rate of 1 radian/sec using a parallel plate geometry (under nitrogen).
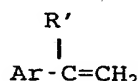
These properties are necessary in order to achieve successful replication. If these properties are not achieved, the pit(s) or groove cannot be adequately formed and will not have the integrity

30   required at such data densities.

The high density optical media disc of the present invention is typically produced from a material which is additionally substantially transparent. The transparency of the material should be such that the light transmittance of the disc substrate at a wavelength of greater than 390 nm to 700 nm is greater than 80 percent.

35   Polymers which can be used in producing the discs of the present invention include saturated hydrocarbon thermoplastics. The term saturated refers to the amount of olefinic bonds within the chemical structure. As used herein, saturated refers to a polymer wherein less than 10 percent of the carbon-carbon bonds are olefinic or unsaturated in nature, preferably less than 7.5 percent, more preferably less than 5 percent, even more preferably less than 2 percent, and most preferably less than

1.5 percent. These types of polymers include hydrogenated aromatic/conjugated diene block copolymers, cyclic-olefin-copolymers and hydrogenated ring opening metathesis polymers and blends thereof.

Aromatic/conjugated diene block copolymers include block copolymers of a vinyl aromatic
5   monomer and a conjugated diene monomer. The vinyl aromatic monomer is typically a monomer of the formula:

$$\begin{array}{c} R' \\ | \\ Ar\text{-}C\text{=}CH_2 \end{array}$$

10

wherein R' is hydrogen or alkyl, Ar is phenyl, halophenyl, alkylphenyl, alkylhalophenyl, naphthyl, pyridinyl, or anthracenyl, wherein any alkyl group contains 1 to 6 carbon atoms which may be mono or multisubstituted with functional groups such as halo, nitro, amino, hydroxy, cyano, carbonyl and carboxyl. More preferably Ar is phenyl or alkyl phenyl with phenyl being most preferred. Typical vinyl
15   aromatic monomers include styrene, alpha-methylstyrene, all isomers of vinyl toluene, especially paravinyltoluene, all isomers of ethyl styrene, propyl styrene, butyl styrene, vinyl biphenyl, vinyl naphthalene, vinyl anthracene and the like, and mixtures thereof. Block copolymers containing 5 or more blocks can contain more than one specific polymerized vinyl aromatic monomer. In other words, for example, a pentablock copolymer can contain a polystyrene block and a poly-alpha-methylstyrene
20   block. The hydrogenated vinyl aromatic polymer block may also be a copolymer of a vinyl aromatic wherein the vinyl aromatic portion is at least 50 weight percent of the copolymer. Preferably, the vinyl aromatic polymer block is a styrene polymer block.

The conjugated diene monomer can be any monomer having two conjugated double bonds. Such monomers include for example 1,3-butadiene, 2-methyl-1,3-butadiene, 2-methyl-1,3 pentadiene,
25   isoprene and similar compounds, and mixtures thereof. Preferably, the conjugated diene is a butadiene.

The conjugated diene polymer block can be prepared from materials which remain amorphous after the hydrogenation process, or materials which are capable of crystallization after hydrogenation. Hydrogenated polyisoprene blocks remain amorphous, while hydrogenated polybutadiene blocks can
30   be either amorphous or crystallizable depending upon their structure. Polybutadiene can contain either a 1,2 configuration, which hydrogenates to give the equivalent of a 1-butene repeat unit, or a 1,4-configuration, which hydrogenates to give the equivalent of an ethylene repeat unit. Polybutadiene blocks having at least approximately 40 weight percent 1,2-butadiene content, based on the weight of the polybutadiene block, provides substantially amorphous blocks with low glass transition
35   temperatures upon hydrogenation. Polybutadiene blocks having less than approximately 40 weight percent 1,2-butadiene content, based on the weight of the polybutadiene block, provide crystalline blocks upon hydrogenation. It may be desirable to incorporate a crystalline block (to improve solvent resistance) or an amorphous, more compliant block. One way of achieving low birefringence is in the control of the 1,2 to 1,4 content of the polybutadiene block. In one embodiment, the weight ratio of 1,2
40   to 1,4 content of the polybutadiene block is greater than 20:80, generally greater than 25:75, preferably

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greater than 30:70, and more preferably greater than 35:65. In cases where the weight ratio of 1,2 to 1,4 content of the polybutadiene block is 1:5 or less, the birefringence can be controlled by incorporating a hydrogenated polybutadiene polymer block having generally 120 monomer units or less, typically 115 monomer units or less, characteristically 110 monomer units or less, preferably 105

5   monomer units or less, more preferably 95 monomer units or less, even more preferably 90 monomer units or less and most preferably 85 monomer units or less.

In some applications, the block copolymer can contain more than one conjugated diene polymer block, such as a polybutadiene block and a polyisoprene block. The conjugated diene polymer block may also be a copolymer of a conjugated diene, wherein the conjugated diene portion of

10   the copolymer is at least 50 weight percent of the copolymer.

Other polymeric blocks may also be included in the vinyl aromatic/conjugated diene block copolymers.

A block is herein defined as a polymeric segment of a copolymer which exhibits microphase separation from a structurally or compositionally different polymeric segment of the copolymer.

15   Microphase separation occurs due to the incompatibility of the polymeric segments within the block copolymer. Microphase separation and block copolymers are widely discussed in "Block Copolymers- Designer Soft Materials", PHYSICS TODAY, February, 1999, pages 32-38.

The hydrogenated block copolymers typically contain from 65 to 90 weight percent of a hydrogenated vinyl aromatic polymer, for example, polyvinylcyclohexane or PVCH block, preferably

20   from 70, more preferably from 75, to 90 weight percent, preferably to 85, based on the total weight of the hydrogenated block copolymer.

The hydrogenated block copolymers of the present invention typically contain from 10 to 35 weight percent of a hydrogenated conjugated diene polymer block, preferably from 12, to 30 weight percent, preferably to 25, more preferably to 20, based on the total weight of the copolymer.

25   The hydrogenated block copolymers are produced by the hydrogenation of block copolymers including triblock, multiblock, tapered block, and star block copolymers such as SBS, SBSBS, SIS, SISIS, and SISBS (wherein S is polystyrene, B is polybutadiene and I is polyisoprene). The block copolymers contain at least one triblock segment comprised of a vinyl aromatic polymer block on each end. The block copolymers may, however, contain any number of additional blocks, wherein these

30   blocks may be attached at any point to the triblock polymer backbone. Thus, linear blocks would include for example SBS, SBSB, SBSBS, and SBSBSB. The copolymer can also be branched, wherein polymer chains are attached at any point along the copolymer backbone.

The total number average molecular weight (Mn_t) of the hydrogenated block copolymers is typically from 30,000, preferably from 32,000, more preferably from 35,000 and most preferably from

35   40,000 to 70,000, preferably to 68,000, more preferably to 65,000. Number average molecular weight (Mn) as referred to throughout this application is determined using gel permeation chromatography (GPC). The molecular weight of the hydrogenated block copolymer and properties obtained are dependent upon the molecular weight of each of the hydrogenated polymeric blocks. It has been discovered that by optimizing the molecular weight of the hydrogenated polymeric blocks,

40   hydrogenated block copolymers of low molecular weight (30,000 to 70,000) can achieve high heat

distortion temperatures and excellent toughness and tensile strength properties. Surprisingly, we have found that good physical properties can be obtained at relatively low hydrogenated block copolymer molecular weights which gives superior processability.

5   Methods of making block copolymers are well known in the art. Typically, block copolymers are made by anionic polymerization, examples of which are cited in Anionic Polymerization: Principles and Practical Applications, H.L. Hsieh and R.P. Quirk, Marcel Dekker, New York, 1996. In one embodiment, block copolymers are made by sequential monomer addition to a carbanionic initiator such as sec-butyl lithium or n-butyl lithium. In another embodiment, the copolymer is made by coupling a triblock material with a divalent coupling agent such as 1,2-dibromoethane, dichlorodimethylsilane, or

10   phenylbenzoate. In this embodiment, a small chain (less than 10 monomer repeat units) of a conjugated diene polymer can be reacted with the vinyl aromatic polymer coupling end to facilitate the coupling reaction. Vinyl aromatic polymer blocks are typically difficult to couple, therefore, this technique is commonly used to achieve coupling of the vinyl aromatic polymer ends. The small chain of diene polymer does not constitute a distinct block since no microphase separation is achieved.

15   Coupling reagents and strategies which have been demonstrated for a variety of anionic polymerizations are discussed in Hsieh and Quirk, Chapter 12, pgs. 307-331. In another embodiment, a difunctional anionic initiator is used to initiate the polymerization from the center of the block system, wherein subsequent monomer additions add equally to both ends of the growing polymer chain. An example of a such a difunctional initiator is 1,3-bis(1-phenylethenyl) benzene treated with organolithium

20   compounds, as described in U.S. Patents 4,200,718 and 4,196,154.

         After preparation of the block copolymer, the copolymer is hydrogenated to remove sites of unsaturation in both the conjugated diene polymer block and the vinyl aromatic polymer block segments of the copolymer. Any method of hydrogenation can be used and such methods typically include the use of metal catalysts supported on an inorganic substrate, such as Pd on $BaSO_4$ (U.S.

25   Patent 5,352,744) and Ni on kieselguhr (U.S. Patent 3,333,024). Additionally, soluble, homogeneous catalysts such those prepared from combinations of transition metal salts of 2-ethylhexanoic acid and alkyl lithiums can be used to fully saturate block copolymers, as described in Die Makromolekulare Chemie, Volume 160, pp. 291, 1972. The copolymer hydrogenation can also be achieved using hydrogen and a heterogeneous catalyst such as those described in U.S. patents 5,352,744, U.S.

30   5,612422 and U.S. 5,645,253. The catalysts described therein are heterogeneous catalysts consisting of a metal crystallite supported on a porous silica substrate. An example of a silica supported catalyst which is especially useful in the polymer hydrogenation is a silica which has a surface area of at least 10 m^2/g and which is synthesized such that it contains pores with diameters ranging between 3000 and 6000 angstroms. This silica is then impregnated with a metal capable of catalyzing hydrogenation of

35   the polymer, such as nickel, cobalt, rhodium, ruthenium, palladium, platinum, other Group VIII metals, combinations or alloys thereof. Other heterogeneous catalysts can also be used, having diameters in the range of 500 to 3,000 angstroms.

         Alternatively, the hydrogenation can be conducted in the presence of a mixed hydrogenation catalyst characterized in that it comprises a mixture of at least two components. The first component

40   comprises any metal which will increase the rate of hydrogenation and includes nickel, cobalt, rhodium,

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ruthenium, palladium, platinum, other Group VIII metals, or combinations thereof. Preferably rhodium and/or platinum is used. However, platinum is known to be a poor hydrogenation catalyst for nitriles, therefore, platinum would not be preferred in the hydrogenation of nitrile copolymers. The second component used in the mixed hydrogenation catalyst comprises a promoter which inhibits deactivation

5   of the Group VIII metal(s) upon exposure to polar materials, and is herein referred to as the deactivation resistant component. Such components preferably comprise rhenium, molybdenum, tungsten, tantalum or niobium or mixtures thereof.

The amount of the deactivation resistant component is at least an amount which significantly inhibits the deactivation of the Group VIII metal component when exposed to polar impurities within a

10   polymer composition, herein referred to as a deactivation inhibiting amount. Deactivation of the Group VIII metal is evidenced by a significant decrease in hydrogenation reaction rate. This is exemplified in comparisons of a mixed hydrogenation catalyst and a catalyst containing only a Group VIII metal component under identical conditions in the presence of a polar impurity, wherein the catalyst containing only a Group VIII metal component exhibits a hydrogenation reaction rate which is less than

15   75 percent of the rate achieved with the mixed hydrogenation catalyst.

Preferably, the amount of deactivation resistant component is such that the ratio of the Group VIII metal component to the deactivation resistant component is from 0.5:1 to 10:1, more preferably from 1:1 to 7:1, and most preferably from 1:1 to 5:1.

The catalyst can consist of the components alone, but preferably the catalyst additionally

20   comprises a support on which the components are deposited. In one embodiment, the metals are deposited on a support such as a silica, alumina or carbon. In a more specific embodiment, a silica support having a narrow pore size distribution and surface area greater than 10 meters squared per gram (m^2/g) is used.

The pore size distribution, pore volume, and average pore diameter of the support can be

25   obtained via mercury porosimetry following the proceedings of ASTM D-4284-83.

The pore size distribution is typically measured using mercury porosimetry. However, this method is only sufficient for measuring pores of greater than 60 angstroms. Therefore, an additional method must be used to measure pores less than 60 angstroms. One such method is nitrogen desorption according to ASTM D-4641-87 for pore diameters of less than about 600 angstroms.

30   Therefore, narrow pore size distribution is defined as the requirement that at least 98 percent of the pore volume is defined by pores having pore diameters greater than 300 angstroms and that the pore volume measured by nitrogen desorption for pores less than 300 angstroms, be less than 2 percent of the total pore volume measured by mercury porosimetry.

The surface area can be measured according to ASTM D-3663-84. The surface area is

35   typically between 10 and 100 m^2/g, preferably between 15 and 90 with most preferably between 50 and 85 m^2/g.

The desired average pore diameter is dependent upon the polymer which is to be hydrogenated and its molecular weight (Mn). It is preferable to use supports having higher average pore diameters for the hydrogenation of polymers having higher molecular weights to obtain the desired amount of

40   hydrogenation. For high molecular weight polymers (Mn>200,000 for example), the typical desired

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surface area can vary from 15 to 25 m^2/g and the desired average pore diameter from 3,000 to 4000 angstroms. For lower molecular weight polymers ($Mn<100,000$ for example), the typical desired surface area can vary from 45 to 85 m^2/g and the desired average pore diameter from 300 to 700 angstroms.

5   Silica supports are preferred and can be made by combining potassium silicate in water with a gelation agent, such as formamide, polymerizing and leaching as exemplified in U.S. Patent No. 4,112,032. The silica is then hydrothermally calcined as in Iler, R.K., The Chemistry of Silica, John Wiley and Sons, 1979, pp. 539-544, which generally consists of heating the silica while passing a gas saturated with water over the silica for about 2 hours or more at temperatures from 600°C to 850°C.
10   Hydrothermal calcining results in a narrowing of the pore diameter distribution as well as increasing the average pore diameter. Alternatively, the support can be prepared by processes disclosed in Iler, R.K., The Chemistry of Silica, John Wiley and Sons, 1979, pp. 510-581.

       A silica supported catalyst can be made using the process described in U.S. Patent No. 5,110,779. An appropriate metal, metal component, metal containing compound or mixtures thereof,
15   can be deposited on the support by vapor phase deposition, aqueous or nonaqueous impregnation followed by calcination, sublimation or any other conventional method, such as those exemplified in Studies in Surface Science and Catalysis, "Successful Design of Catalysts" V. 44, pg. 146-158, 1989 and Applied Heterogeneous Catalysis pgs. 75-123, Institute Français du Pétrole Publications, 1987. In methods of impregnation, the appropriate metal containing compound can be any compound
20   containing a metal, as previously described, which will produce a usable hydrogenation catalyst which is resistant to deactivation. These compounds can be salts, coordination complexes, organometallic compounds or covalent complexes.

       Typically, the total metal content of the supported catalyst is from 0.1 to 10 wt. percent based on the total weight of the silica supported catalyst. Preferable amounts are from 2 to 8 wt. percent, more
25   preferably 0.5 to 5 wt. percent based on total catalyst weight.

       Promoters, such as alkali, alkali earth or lanthanide containing compounds, can also be used to aid in the dispersion of the metal component onto the silica support or stabilization during the reaction, though their use is not preferred.

       The amount of supported catalyst used in the hydrogenation process is much smaller than the
30   amount required in conventional unsaturated polymer hydrogenation reactions due to the high reactivity of the hydrogenation catalysts. Generally, amounts of less than 1 gram of supported catalyst per gram of unsaturated polymer are used, with less than 0.1 gram being preferred and less than 0.05 being more preferred. The amount of supported catalyst used is dependent upon the type of process, whether it is continuous, semi-continuous or batch, and the process conditions, such as temperature,
35   pressure and reaction time wherein typical reaction times may vary from 5 minutes to 5 hours. Continuous operations can typically contain 1 part by weight supported catalyst to 200,000 or more parts unsaturated polymer, since the supported catalyst is reused many times during the course of continuous operation. Typical batch processes can use 1 part by weight supported catalyst to 5,000 parts unsaturated polymer. Higher temperatures and pressures will also enable using smaller amounts
40   of supported catalyst.

The hydrogenation reaction can be conducted in the absence of a solvent but is preferably conducted in a hydrocarbon solvent in which the polymer is soluble and which will not hinder the hydrogenation reaction. Preferably the solvent is a saturated solvent such as cyclohexane, methylcyclohexane, ethylcyclohexane, cyclooctane, cycloheptane, dodecane, dioxane, diethylene

5   glycol dimethyl ether, tetrahydrofuran, isopentane, decahydronaphthalene or mixtures thereof, with cyclohexane being the most preferred.

The temperature at which the hydrogenation is conducted can be any temperature at which hydrogenation occurs without significant degradation of the polymer. Degradation of the polymer can be detected by a decrease in Mn, an increase in polydispersity or a decrease in glass transition

10   temperature, after hydrogenation. Significant degradation in polymers having a polydispersity between 1.0 and 1.2 can be defined as an increase of 30 percent or more in polydispersity after hydrogenation. Preferably, polymer degradation is such that less than a 20 percent increase in polydispersity occurs after hydrogenation, most preferably less than 10 percent. In polymers having polydispersity greater than about 1.2, a significant decrease in molecular weight after hydrogenation indicates that

15   degradation has occurred. Significant degradation in this case is defined as a decrease in Mn of 20 percent or more. Preferably, a Mn decrease after hydrogenation will be less than 10 percent. However, polymers such as poly-alpha-methylstyrene or other alpha substituted vinyl aromatic polymers which are more prone to polymer degradation, can tolerate a decrease in Mn of up to 30 percent.

20   Typical hydrogenation temperatures are from 40°C preferably from 100°C, more preferably from 110°C, and most preferably from 120°C to 250°C, preferably to 200°C, more preferably to 180°C, and most preferably to 170°C.
The pressure of the hydrogenation reaction is not critical, though hydrogenation rates increase with increasing pressure. Typical pressures range from atmospheric pressure to 70 MPa, with 0.7 to 10.3

25   MPa being preferred.

The reaction vessel is purged with an inert gas to remove oxygen from the reaction area. Inert gases include but are not limited to nitrogen, helium, and argon, with nitrogen being preferred.

The hydrogenating agent can be any hydrogen producing compound which will efficiently hydrogenate the unsaturated polymer. Hydrogenating agents include but are not limited to hydrogen

30   gas, hydrazine and sodium borohydride. In a preferred embodiment, the hydrogenating agent is hydrogen gas.

The amount of olefinic hydrogenation can be determined using Infrared or proton NMR techniques. The amount of aromatic hydrogenation can be measured using UV-VIS spectroscopy. Cyclohexane solutions of polystyrene give a very distinct absorption band for the aromatic ring at about

35   260.5 nm. This band gives an absorbance of 1.000 with a solution concentration of .004980 moles of aromatic per liter in a 1 cm cell. After removing the catalyst via filtration (using a 0.50 micrometer (μm) "TEFLON™" filter, Millipore FHUP047) the reaction mixture is placed in a UV cell and the absorbance measured. The absorbance is dependent upon concentration. The hydrogenated polymer products are typically measured at higher concentrations since they are not diluted before the absorbance is

measured. Since the reaction solution is about 15 to 30 times more concentrated than the standards, small amounts of residual unsaturation can be accurately measured.

The level of hydrogenation of the block copolymer is preferably greater than 95 percent of the conjugated diene polymer block and greater than 90 percent of the vinyl aromatic polymer block

5   segments, more preferably greater than 99 percent of the conjugated diene polymer block and greater than 95 percent of the vinyl aromatic polymer block segments, even more preferably greater than 99.5 percent of the conjugated diene polymer block and greater than 98 percent of the vinyl aromatic polymer block segments, and most preferably greater than 99.9 percent of the conjugated diene polymer block and 98.5 percent of the vinyl aromatic polymer block segments. The term 'level of

10   hydrogenation' refers to the percentage of the original unsaturated bonds which become saturated upon hydrogenation. The level of hydrogenation in hydrogenated vinyl aromatic polymers is determined using UV-VIS spectrophotometry, while the level of hydrogenation in hydrogenated diene polymers is determined using proton NMR.

Additionally, blends of different hydrogenated vinyl aromatic/conjugated diene block

15   copolymers can be used to produce the high density discs of the present invention.

Cyclic-olefin-copolymers are copolymerized cycloolefin monomers with other acyclic or cyclic olefin comonomers. Cyclic-olefin-copolymers include norbornene-type polymers as described in U.S. Patent Nos. 5,115,041, 5,142,007, 5,143,979. The cycloolefin moiety may be substituted or unsubstituted. Suitable cycloolefin monomers include substituted and unsubstituted norbornenes,

20   dicyclopentadienes, dihydrodicyclopentadienes, trimers of cyclopentadiene, tetracyclododecenes, hexacycloheptadecenes, ethylidenyl norbornenes and vinylnorbornenes. Substituents on the cycloolefin monomers include hydrogen, alkyl alkenyl, and aryl groups of 1 to 20 carbon atoms and saturated and unsaturated cyclic groups of 3 to 12 carbon atoms which can be formed with one or more, preferably two, ring carbon atoms. Generally speaking, the substituents on the cycloolefin

25   monomers can be any which do not poison or deactivate the polymerization catalyst. Examples of preferred monomers include but are not limited to dicyclopentadiene, methyltetracyclododecene, 2-norbornene, and other norbornene monomers such as 5-methyl-2-norbornene, 5,6-dimethyl-2-norbornene, 5-ethyl-2-norbornene, 5-ethylidenyl-2-norbornene, 5-butyl-2-norbornene, 5-hexyl-2-norbornene, 5-octyl-2-norbornene, 5-phenyl-2-norbornene, 5-dodecyl-2-norbornene, 5-isobutyl-2-

30   norbornene, 5-octadecyl-2-norbornene, 5-isopropyl-2-norbornene, 5-p-toluyl-2-norbornene, 5-α-naphthyl-2-norbornene, 5-cyclohexyl-2-norbornene, 5-isopropenyl-2-norbornene, 5-vinyl-2-norbornene, 5,5-dimethyl-2-norbornene, tricyclopentadiene (or cyclopentadiene trimer), tetracyclopentadiene (or cyclopentadiene tetramer), dihydrodicyclopentadiene (or cyclopentene-cyclopentadiene co-dimer), methyl-cyclopentadiene dimer, ethyl-cyclopentadiene dimer, tetracyclododecene 9-methyl-

35   tetracyclo$[6,2,1,1^{3,6}O^{2,7}]$dodecene-4, (or methyl-tetracyclododecene), 9-ethyl-tetracyclo$[6,2,1,1^{3,6}O^{2,7}]$dodecene-4, (or ethyl-tetracyclododecene), 9-hexyl-tetracyclo$[6,2,1,1^{3,6}O^{2,7}]$dodecene-4, 9-decyl-tetracyclo-$[6,2,1,1^{3,6}O^{2,7}]$dodecene-4, 9-decyl-tetracyclo$[6,2,1,1^{3,6}O^{2,7}]$dodecene-4, 9,10-dimethyl-tetracyclo$[6,2,1,1^{3,6}O^{2,7}]$dodecene-4, 9-methyl-10-ethyl-tetracyclo$[6,2,1,1^{3,6}O^{2,7}]$dodecene-4, 9-cyclohexyl-tetracyclo-$[6,2,1,1^{3,6}O^{2,7}]$dodecene-4, 9-chloro-

40   tetracyclo$[6,2,1,1^{3,6}O^{2,7}]$dodecene-4, 9-bromo-tetracyclo$[6,2,1,1^{3,6}O^{2,7}]$dodecene-4, 9-fluoro-tetracyclo-

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[6,2,1,1^{3,6}O^{2,7}]dodecene-4, 9-isobutyl-tetracyclo[6,2,1,1^{3,6}O^{2,7}]dodecene-4, and 9,10-dichloro tetracyclo[6,2,1,1^{3,6}O^{2,7}]dodecene-4. Acyclic olefin comonomers are typically olefins such as ethylene, and propylene.

Polymers comprising two or more different cyclic types of monomeric units are also suitable. For example, copolymers of methyltetra-cyclododecane (MTD) and methylnorbornene (MNB) are especially suitable. More preferably, the polymers comprise three or more different types of monomeric units, for example, terpolymers, including MTD, MNB and dicyclopentadiene (DCPD).

Ring opening metathesis polymers include polymers prepared by metathesis ring opening (co)polymerization of a norbornene or tetracyclododecene, such as those described in JP-85/26,024 and U.S. Patent No. 5,053,471. Methods of hydrogenating such polymers are well known by those skilled in the art.

Other additives may also be included in the above identified polymer compositions including heat stabilizers, mold release agents, flow aids, UV stabilizers, and processing aids such as mineral oil. Polymer blends can also be used, such as blends of hydrogenated vinyl aromatic homopolymer blended with hydrogenated vinyl aromatic/conjugated diene block copolymer, and blends of different hydrogenated block copolymers.

Discs can be molded using any molding technique such as those described in The Compact Disc Handbook, 2nd edition, by Pohlmann.

Methods of molding optical media discs are well known in the art and include injection-compression molding. A preferred method includes injection compression-molding as described in Injection Molding An Introduction, pgs. 171-172 Hanser/Gardner/ Publication, Inc., Cincinnati, 1995 by Potsch and Michaeli. Discs are molded using a stamper which 'transfers' the format specific surface features into the disc at the designated density. Format specific surface features include a pit in the case of pre-recorded formats and a groove which is capable of holding information in the case of rewritables. The stamper utilized will have a density of at least 7.5 Gb. High data densities in prerecorded formats can be achieved by numerous known methods including positioning surface features in closer relation to each other, decreasing the pit angle and obtaining multiple pit depths as well. One reason such discs have not been contemplated previously is that prior art materials require mold release agents and therefore would be even more difficult to use at higher densities or very low track pitches.

The following examples are provided to illustrate the present invention. The examples are not intended to limit the scope of the present invention and they should not be so interpreted. Amounts are in weight parts or weight percentages unless otherwise indicated.

EXAMPLES

I) Procedure for preparing Block Copolymer Sample 1

Sequential Polymerization of Pentablock Copolymer

A mixture of 386 Kg of cyclohexane containing approximately 8 to 15 weight percent isopentane is added to a 1136 liter stirred reactor under nitrogen atmosphere. The reactor is blanked by adding 0.5 Kg of a cyclohexane solution which is 0.0979 molar in low molecular weight polystyryl lithium. To this mixture is added 1.08 liters of a 1.4M solution of sec-butyllithium in cyclohexane. The

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solution is heated to approximately 65°C and 22.6 Kg of styrene monomer is added, followed by a 34 Kg hydrocarbon solvent purge of the styrene line. After 20 minutes of polymerization, 11.3 Kg of butadiene monomer is added at a temperature of about 70°C, followed by 34 Kg of hydrocarbon solvent which is followed immediately by another styrene addition of 22.6 Kg. After another 20

5 minutes, a second addition of 11.3 Kg of butadiene is made at about 70°C, followed by a 34 Kg line flush with solvent. After another 20 minutes, the third addition of 22.6 Kg of styrene is made and the polymerization continues for a final 20 minutes. At this point 114 grams of 2-propanol is added to terminate the reaction.

Table 1

10

Sample	Actual	Actual	Actual % Polystyrene	Actual % Polybutadiene	Actual % 1,2
	Mp*	Mw/Mn	before hydrogenation	before hydrogenation	Content
1	62000	1.03	71	29	11

*Mp is peak Molecular weight.

The block copolymer is then hydrogenated such that all of the polybutadiene block and polystyrene blocks are completely saturated.

15 II) Hydrogenation

Approximately 20 grams of a dried block copolymer is dissolved in 700 mL cyclohexane. This polymer is hydrogenated using a Pt on SiO_2 hydrogenation catalyst as described in U.S. Patent No. 5,612,422. The polymer to catalyst ratio is 10 to 1. The hydrogenation reaction is conducted in a PPI (Precision Pressure Industry) reactor for 12 hours at 177°C under 3447 MPa hydrogen.

20 Table 2 shows a series of physical properties for the hydrogenated block copolymer. Mechanical properties are obtained using compression molded samples. Tensile properties are measured according to ASTM D638 using type 5 microtensile specimens at a crosshead speed of 0.127cm/min. and a 101.9 Kg load cell.

Table 2

Sample.	Tensile Yield (MPa)	Tensile Rupture (MPa)	Tensile Modulus (MPa)	Complex Viscosity (poise)
1	29.6	30.3	1,860	5.24×10^4

25

High Density DVD Example

A DVD substrate is injection compression molded from the hydrogenated block copolymer of Sample 1, using an injection/compression molding machine with a maximum clamping force 600kN, maximum injection stroke capability of 100mm and injection screw diameter of 32mm. The substrate

30 mold is a DVD single cavity substrate mold. Optical discs are prepared using a data bearing stamper which is inserted into the mold and contains approximately 15 Gb of data, and track pitch of 0.4 to 0.5 microns. Process temperatures are melt temperatures of 290 to 330°C, and mold temperatures of 40 to 80°C. Injection velocity is varied from 25 mm/s to 200 mm/s, increasing as the mold is filled. Once filled, the part is further packed with polymer by applying initial hold pressure of approximately 300 bar

35 which is then reduced to 0 bar over a period of 0.8 sec. The polymer injection shot size is

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approximately 13.5 mm to achieve a completely full part with an actual part thickness of 0.6 mm. The compression phase is accomplished by applying 55 to -65 percent clamp force to the injection mold at the time when approximately 85 percent of the polymer shot has been injected into the mold cavity. Prior to compression the mold cavity is typically between 1.0 and 1.2 mm thick. The overall cycle time for the process including part removal is 5 to 10 seconds. The DVD substrates are 120 mm in diameter and 0.6 mm thick.

Once molded, the DVD substrates are sputtered with an aluminum reflective layers. Two individual substrates are bonded together to form a dual layer 30 Gb disc.

CLAIMS:

1.   A high data density pre-recorded optical media disc having a data density of at least 7.5 Gigabytes per disc layer or 0.17 Gigabytes per square cm (Gb/cm^2) per layer and a degree of replication such that the average pit depth equals 1/4 to 1/8 times (the wavelength of the laser divided by the refractive index of the disc) and wherein the disc has a retardation of less than 25 nm per 0.6 mm substrate thickness, and a water absorbance of less than 0.5 % as measured according to ASTM D570.

2.   The disc of Claim 1 having a data density of at least 0.2 Gb/cm^2 per layer.

3.   The disc of Claim 1, wherein the light transmittance of the disc is at least 80 percent at a wavelength of greater than 390 nm to 700 nm.

4.   The disc of Claim 1, wherein the pit depth is equal to 1/4 to 1/6 times (the laser wavelength divided by the refractive index of the disc.

5.   A high data density rewritable optical media disc having a data density of at least 0.05 Gb/cm^2, wherein at least 75 percent replication is achieved as measured by a combination of groove height and left and right sidewall angles, and wherein the disc has a retardation of less than 25 nm per 0.6 mm substrate thickness, and a water absorbance of less than 0.5 percent as measured according to ASTM D570.

6.   The disc of Claim 5 having a data density of at least 0.08 Gb/cm^2.

7.   The disc of Claim 5, wherein the light transmittance of the disc is at least 80 percent at a wavelength of greater than 390 nm to 700 nm.

8.   The disc of Claim 1 or 5 produced from a polymer having:

a glass transition temperature (Tg) of greater than 110°C as measured by Differential Scanning Calorimetry (DSC) at 10°C/min.,

an elastic modulus (G') of less than 1000 dynes/cm^2 at a temperature of 240°C as measured by Dynamic Mechanical Spectroscopy measurements at a temperature ramp rate of 3°C/min., and a shear rate of 1 radian/sec using a parallel plate geometry (under nitrogen), and

a complex viscosity (Eta*) of less than 2000 poise as measured according to Dynamic Mechanical Spectroscopy measurements, using shear rate sweeps at 280°C, and a shear rate of 1 radian/sec using a parallel plate geometry (under nitrogen).

9.   The disc of Claim 8, wherein the retardation is less than 20 nm.

10.   The disc of Claim 8, wherein the polymer comprises a saturated hydrocarbon thermoplastic.

11.   The disc of Claim 10, wherein the saturated hydrocarbon thermoplastic comprises a hydrogenated vinyl aromatic/conjugated diene block copolymer.

12.   The optical media disc of Claim 11, wherein the block copolymer comprises at least two distinct blocks of hydrogenated polymerized vinyl aromatic monomer, herein referred to as hydrogenated vinyl aromatic polymer block, and at least one block of hydrogenated polymerized

butadiene monomer, herein referred to as hydrogenated butadiene polymer block, wherein the hydrogenated block copolymer is characterized by:

    1)   a hydrogenation level such that each hydrogenated vinyl aromatic polymer block has a hydrogenation level of greater than 90 percent and each hydrogenated conjugated diene polymer block

5   has a hydrogenation level of greater than 95 percent, and

    2a)   a weight ratio of 1,2 to 1,4 polybutadiene content of greater than 20:80, or

    2b)   a hydrogenated butadiene polymer block comprising 120 monomer units or less.

    13.   The disc of Claim 11, wherein the vinyl aromatic monomer is styrene.

    14.   The disc of Claim 11, wherein the butadiene polymer block has a weight ratio of 1,2 to

10   1,4 polybutadiene content of greater than 25:75.

    15.   The disc of Claim 14, wherein the weight ratio of 1,2 to 1,4 polybutadiene content is greater than 30:70.

    16.   The disc of Claim 11, wherein the vinyl aromatic/conjugated diene block copolymer comprises a hydrogenated isoprene polymer block.

15   17.   The disc of Claim 8, wherein the polymer comprises a cyclic olefin copolymer.

    18.   The disc of Claim 8, wherein the polymer comprises a hydrogenated ring opening metathesis polymer.

    19.   A method of producing a high data density pre-recorded optical media disc having a data density of at least 7.5 Gigabytes per disc layer or 0.17 Gigabytes per square cm (Gb/cm^2) per

20   layer and a degree of replication such that the average pit depth equals 1/4 to 1/8 times (the wavelength of the laser divided by the refractive index of the disc); or a rewritable optical media disc having a data density of at least 0.05 Gb/cm^2, wherein at least 75% replication is achieved as measured by a combination of groove height and the left and right sidewall angles, and wherein the pre-recorded or rewritable disc has a retardation of less than 25 nm per 0.6 mm substrate thickness,

25   and a water absorbance of less than 0.5% as measured according to ASTM D570, comprising compression injection molding a polymer having a glass transition temperature (Tg) of greater than 110°C as measured by Differential Scanning Calorimetry (DSC) at 10°C/min.,

    an elastic modulus (G') of less than 1000 dynes/cm^2 at a temperature of 240°C as measured by Dynamic Mechanical Spectroscopy measurements at a temperature ramp rate of 3°C/min., and a

30   shear rate of 1 radian/sec using a parallel plate geometry (under nitrogen), and

    a complex viscosity (Eta*) of less than 2000 poise as measured according to Dynamic Mechanical Spectroscopy measurements, using shear rate sweeps at 280°C, and a shear rate of 1 radian/sec using a parallel plate geometry (under nitrogen),

    into a high density optical media disc mold.

35   20.   The method of Claim 19 wherein the retardation is less than 20 nm.

    21.   The method of Claim 20 wherein the polymer comprises a saturated hydrocarbon thermoplastic.

    22.   The method of Claim 21, wherein the saturated hydrocarbon thermoplastic comprises a hydrogenated vinyl aromatic/conjugated diene block copolymer.

23.   The method of Claim 22 wherein the block copolymer comprises at least two distinct blocks of hydrogenated polymerized vinyl aromatic monomer, herein referred to as hydrogenated vinyl aromatic polymer block, and at least one block of hydrogenated polymerized butadiene monomer, herein referred to as hydrogenated butadiene polymer block, wherein the hydrogenated block
5   copolymer is characterized by:

1)   a hydrogenation level such that each hydrogenated vinyl aromatic polymer block has a hydrogenation level of greater than 90 percent and each hydrogenated conjugated diene polymer block has a hydrogenation level of greater than 95 percent, and

2a)   a weight ratio of 1,2 to 1,4 polybutadiene content of greater than 20:80, or
10   2b)   a hydrogenated butadiene polymer block comprising 120 monomer units or less.

24.   The method of Claim 22, wherein the vinyl aromatic monomer is styrene.

25.   The method of Claim 22, wherein the butadiene polymer block has a weight ratio of 1,2 to 1,4 polybutadiene content of greater than 25:75.

26.   The method of Claim 25, wherein the weight ratio of 1,2 to 1,4 polybutadiene content
15   is greater than 30:70.

27.   The method of Claim 22, wherein the hydrogenated vinyl aromatic/conjugated diene block copolymer comprises a hydrogenated isoprene polymer block.

28.   The method of Claim 19 wherein the polymer comprises a cyclic olefin copolymer.

29.   The method of Claim 19 wherein the polymer comprises a hydrogenated ring opening
20   metathesis polymer.

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7   G11B7/24

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7   G11B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched.

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 505 110 A (MITSUBUSHI KASEI CORPORATION) 23 September 1992 (1992-09-23) column 2, line 50 -column 3, line 24 ----	10,11, 13,16, 21,22, 24,27
A	EP 0 410 468 A (MITSUBISHI KASEI CORPORATION) 30 January 1991 (1991-01-30) page 3, line 10 - line 35 ----	10,11, 13,16, 21,22, 24,27
A	WO 99 17285 A (THE DOW CHEMICAL COMPANY) 8 April 1999 (1999-04-08) page 3, line 6 - line 7 ----	10,11, 21,22

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[X] Further documents are listed in the continuation of box C.   [X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
6 November 2000	1 4. 11. 00

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Gerard, E

Form PCT/ISA/210 (second sheet) (July 1992)

1

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 015, no. 313 (C-0857), 9 August 1991 (1991-08-09) & JP 03 115349 A (MITSUBISHI KASEI CORP), 16 May 1991 (1991-05-16) abstract ---	10,11, 21,22
A	PATENT ABSTRACTS OF JAPAN vol. 1996, no. 07, 31 July 1996 (1996-07-31) & JP 08 072405 A (MITSUBISHI CHEM CORP), 19 March 1996 (1996-03-19) abstract -----	10,21

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INTERNATIONAL SEARCH REPORT

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 1-9, 19, 20
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet (1)) (July 1998)

INTERNATIONAL SEARCH REPORT

FURTHER INFORMATION CONTINUED FROM   PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.:   1-9, 19, 20

Present claims 1 to 7 relate to a product defined by reference to desirable properties, namely a desired data density, a desired degree of replication, a desired retardation, a desired water absorbance and a desired light transmittance.

The claims cover all products having these properties, whereas the application provides support within the meaning of PCT Article 6 and disclosure within the meaning of Article 5 for only a limited group of such products. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Independent of the above reasoning, the claims also lack clarity (PCT Article 6). An attempt is made to define the product by reference to a result to be achieved. Again, this lack of clarity in the present case is such as to render a meaningful search over the whole of the claimed scope impossible. Consequently, the search has been carried out for those parts of the claims which appear to be clear, supported and disclosed, namely those parts relating to the products and method of claims 8 to 29.

Claims 8, 9 and 19, 20 cannot however be searched either. Claims 8, 9 and 19, 20 relate respectively to products and a method defined by reference to the following parameters:

P1: glass transition temperature
P2: elastic modulus
P3: shear rate
P4: complex viscosity

The use of these parameters in the present context is considered to lead to a lack of clarity within the meaning of PCT Article 6. It is impossible to compare all the parameters the applicant has chosen to employ with what is set out in the prior art. The lack of clarity is such as to render a meaning ful complete search impossible. Consequently, the search has been restricted to claims 10 to 18 and 21 to 29.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
EP 505110	A	23-09-1992	JP	2995884 B	27-12-1999
			JP	4288360 A	13-10-1992
			DE	69212677 D	19-09-1996
			DE	69212677 T	02-01-1997
			US	5178926 A	12-01-1993
EP 410468	A	30-01-1991	CA	2022027 A	29-01-1991
			DE	69026768 D	05-06-1996
			DE	69026768 T	19-09-1996
			JP	3130943 A	04-06-1991
			US	5073427 A	17-12-1991
WO 9917285	A	08-04-1999	AU	9301298 A	23-04-1999
			EP	1023723 A	02-08-2000
			US	6030097 A	29-02-2000
JP 03115349	A	16-05-1991	JP	2725402 B	11-03-1998
JP 08072405	A	19-03-1996	NONE		